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Eighth Quarterly Progress Report
April, May and June

to

National Aeronatutics and Space Administration
Washington, D. C.

Contract NASW-90

EXPLORATORY STUDY OF POTASSIUM AND SODIUM SUPEROXIDE FOR OXYGEN CONTROL IN MANNED SPACE VEHICLES

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19 July 1961

MSA Research Corporation

Subsidiary of Mine Safety Appliances Company

Callery, Pennsylvania

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Part 1 - Laboratory Studies

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Part 2 - Chamber Tests, Canister Designs and Animal Studies

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ABSTRACT

Several reactions were tried to prepare pure calcium superoxide. Potassium superoxide was reacted with calcium, calcium oxide, and calcium bromide under different conditions but calcium superoxide was not formed. A solid phase reaction between potassium superoxide and calcium bromide was indicated by the formation of potassium bromide.

Surface area measurements were made on standard, sintered and catalyzed potassium superoxide. The surface area of the standard potassium superoxide was found to be 0.4 m^2/g; sintered was < 0.1 m^2/g and 1% oxychloride-superoxide had an area of 0.6 m^2/g.

In the chamber studies program seven runs were made. One run using sintered potassium superoxide; five runs using regular potassium superoxide at a total system pressure of one-half atmosphere and one run using regular potassium superoxide at atmospheric pressure wherein no cooling or additional water was added to the system other than that formed in the simulator reaction.

These runs showed that sintered potassium superoxide permits more water to be retained in the system and that it can be used to provide a breathable atmosphere for a closed system.

Regular potassium superoxide in a system operating at one-half atmosphere does not require auxiliary equipment to remove carbon dioxide and water.

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on

EXPLORATORY STUDY OF POTASSIUM AND SODIUM SUPEROXIDE FOR OXYGEN CONTROL IN MANNED SPACE VEHICLES

Part 1 - Laboratory Studies

C. A. Palladino

Part 2 - Chamber Tests, Chamber Designs and Animal Studies

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INTRODUCTION

This report covers the period April, May and June, 1961, on Contract NASW-90. Superoxides of sodium and potassium are being studied to better understand the effects of a number of variables on oxygen evolution and carbon dioxide and water absorption.

Other areas studied and reported in this report are the synthesis of calcium superoxide and chamber studies (129 cu ft chamber).

LABORATORY STUDIES

Synthesis of Calcium Superoxide

Potassium superoxide was reacted with calcium metal, calcium oxide, and calcium bromide in five experiments in an attempt to synthesize calcium superoxide. The KO_2 used in the experiments was standard fluff dried at 200°C under vacuum for 2 hr. The $CaBr_2$ and CaO were dried under vacuum at 300°C for 2 hr. Oxide-free Ca was obtained by filing the surface of electrolytic Ca in an argon atmosphere and collecting the filings. Results were evaluated by analyzing the products for superoxide oxygen expressed in cc of oxygen at S.T.P. per gram of material. A superoxide content lower than the KO_2 used would indicate the reaction or decomposition of the KO_2 and little or no CaO_4 formed. A relatively high superoxide content would indicate no change in the KO_2 or the formation of CaO_4. Either case could be confirmed by x-ray diffraction.

Three of the reactions were run in an autoclave, one was run in a sealed glass tube and one in a vacuum system. Table 1 shows the reactants, conditions and results of these runs.

Run No. 1, the reaction of Ca and KO_2 at 360°C and 1600 psig oxygen, resulted in reaction with the nickel container. The black metallic product yielded no superoxide oxygen. Run No. 2 was a repeat of No. 1 at a lower temperature of 300°C. This reaction did not attack the nickel container. The product yielded 35 cc O_2/g superoxide oxygen. In Run No. 3 the KO_2 and CaO mix was placed in a stainless steel container in the autoclave. The container was corroded by the reaction at 300°C and the product yielded 40 cc O_2/g superoxide oxygen.

Run No. 4 was made in a sealed pyrex tube. The sealed tube containing the KO_2 and $CaBr_2$ was placed in a larger diameter vycor tube. The outside tube was heated slowly with a flame. A reaction was observed at 170°C as color changed from KO_2 yellow to white. Heating was continued until the mixture was all white at 330°C. Heating was discontinued and the tube cooled. While cooling, the tube exploded. Some product was collected and the analysis showed 6 cc O_2/g superoxide oxygen. The explosion was probably caused by oxygen pressure from the decomposition of the KO_2.

In Run No. 5, $CaBr_2$ and KO_2 were placed in a pyrex tube which was then sealed to the manifold of a vacuum system. After evacuating the tube for 1 hr the mixture was heated in the same manner as in Run No. 4. The temperature was increased slowly until the color changed from yellow to white at 170°C. Pressure in the system increased to 730 mm Hg, presumably from oxygen evolution. Analysis of the mixture by x-ray diffraction showed the major component to be KBr, small amounts of KO_2, CaO_2, and an unknown component. Formation of KBr shows a solid phase metathesis reaction with KO_2 is possible, however, the temperature at which the reactions were run could have resulted in decomposition of any CaO4 formed.

Calcium superoxide has been shown to decompose very slowly at 200°C.[1] It may be possible to carry out a reaction in a relatively inert medium such as diethyl phthalate in which the temperature could be controlled. Future efforts will be directed towards lower temperature reactions in order to minimize product decomposition and container corrosion problems.

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1 Johnston, R. S., Osgood, E. D., Miller, R. R., Anal. Chem 30, 511 (1958).

Surface Area Measurements

An apparatus was assembled to measure surface area by the continuous flow method.[2] This technique consists of passing a helium-nitrogen stream of known composition over a sample cooled by liquid nitrogen. Nitrogen adsorbed on the sample is released when the coolant is removed and the eluted nitrogen is measured by a thermal conductivity cell. Adsorptions are measured at several nitrogen partial pressures and the standard Brunauer-Emmett-Teller (BET) plot[3] is used to determine the amount of nitrogen required to form a monolayer on the sample surface. This value multiplied by the proper factor for area covered per unit amount of nitrogen gives the surface area expressed in m^2/g.

Table 2 lists the results of the surface area measurements. The results show that KO_2 fluff and granules have a surface area of 0.4 m^2/g. Sintered KO_2 showed no measurable area, which for this apparatus is < 0.1 m^2/g. The low surface area of KO_2 indicates a relatively nonporous structure. Difference in performance between regular and sintered KO_2 was previously attributed to the physical characteristic of porosity. This is substantiated by the surface area measurements.

The higher surface area of 0.6 m^2/g for the catalyzed KO_2 (1% copper oxychloride) could account for the quick starting capability exhibited by this mixture.

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2 Nelsen, F. M., Eggertsen, F. T., Anal. Chem. 30, 1387 (1958).

3 Brunauer, S., Emmett, P. H., Teller, E., J. Am. Chem. Soc. 60, 309 (1938).

Table 1 - Potassium Superoxide Reactions

Run No.	Reactant	(g)	KO_2[1] (g)	Temp. (°C)	O_2 (psig)	Product Superoxide Oxygen (cc O_2/g)
1	Ca	0.7	1.2	360	1600	3
2	Ca	0.3	1.0	300	1600	35
3	CaO	4.0	10.0	300	1600	40
4	$CaBr_2$	1.9	1.3	330	---	6
5	$CaBr_2$	1.9	1.3	170	---	2

1 Starting material yielded 152 cc/g superoxide oxygen.

Table 2 - Surface Area Results

KO_2 Type	Surface Area (m^2/g)
Fluff regular	0.4
2-4 regular	0.4
8-10 regular	0.4
8-10 sintered	<0.1
10-14 1% oxychloride	0.6

CHAMBER STUDIES

INTRODUCTION

Seven runs were made on the system during this quarter. These runs were divided into three parts: Part one was a single run using sintered KO_2 at atmospheric pressure; Part two had a total of five runs using regular KO_2 at a total system pressure of one-half atmosphere, and part three was a single run using only regular KO_2 at atmospheric pressure wherein no cooling was used or water was added to the system other than that formed in the simulator reaction.

DISCUSSION

Part one consisted of using sintered KO_2 in the system. This type of superoxide has an advantage over the regular uncatalyzed chemical in that it has more weight per unit volume. Successful use of it would make it more competitive with other superoxides because it would be less expensive and would require the same or less volume in a system. In addition, it permits the water content of the system to be higher thereby reducing the cooler load, saving weight and volume, and completely eliminating the necessity of using a drier.

Because it is desired to obtain operating data on superoxides at reduced pressure, part two tests were performed wherein the operating pressure was one-half atmosphere. The procedure used consisted of evacuating the system to less than one-half atmosphere, enriching the oxygen partial pressure to 160 mm Hg, removing water from the system, if too much was present, making any necessary adjustments to maintain the one-half atmosphere pressure and then starting the run. The run would be considered complete when either the oxygen content of the system became too low or the CO_2 percentage became too high.

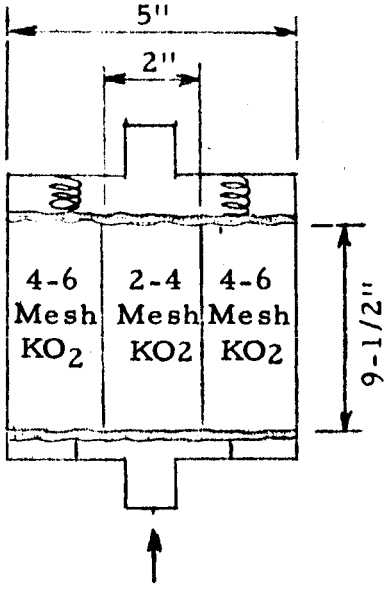
Only one run was made for part three. This was one in which regular KO_2 was used in the system with no cooling and only the water formed in the simulator reaction was added to the system. The purpose was to obtain data such that the reaction characteristics of the KO_2 could be determined, i.e., how KO_2 can produce a certain quantity of oxygen when the chemical absorbs less than the theoretical amount of water required for the reaction and less than the theoretical amount of water is available in the circulating stream through the bed of chemical.

The data for all the runs is given in Table 3 and Fig. 1 shows the canister designs.

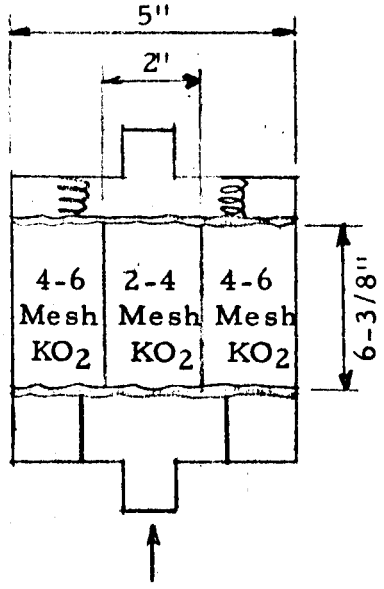
Table 1 - Data Summary for Chamber Study Runs

Data	Run No. 35	36	37	38	39	40	41
Length of run (hr)	4.5	2.45	3.067	5.1	4.5	3.533	3.5
Diameter of bed (in.)	5	5	5	8	5	5	5
Depth of bed (in.)	9-1/2	6-3/8	6-3/8	4-3/4	6-7/8	6-7/8	3
System pressure (mm Hg)	746.6	384	376	364.8	406	435	735.9
System R.Q.	0.8	0.50	0.49	0.52	0.8	0.8	0.8
Weight of chemical (g)	2700	1335	1335	2870	1445	1445	628
Flow through bed (SCFM)	7.15	4.76	4.45	5.43	3.87	4.07	5.25
Flow through bed (lb/hr)	34.6	23.3	21.8	26.6	20.8	20.3	25.4
Apparent velocity (ft/sec)	0.88	0.58	0.54	0.24	0.48	0.50	0.64
Total O_2 evolved (liters)	211.1	213.84	206.9	465.6	284.6	203.0	99.5
Total CO_2 absorbed (liters)	109.5	137.3	146.0	287.5	216.0	153.5	82.2
Total H_2O absorbed (g)	285.4	164.0	119.8	351.8	119.5	143.5	64.7
Chemical efficiency (%)	30.5	67.9	65.7	68.8	83.4	59.7	67.1
Chemical R.Q. (during run)	0.57	0.64	0.71	0.62	0.76	0.76	0.83
Bed inlet H_2O PP (ave. mm Hg)	13	13	9	8	13.6	10.2	8
Bed ΔT ave. (^oF)	13	16	15	20	15	10	6
lb H_2O abs/lb chemical	0.106	0.123	0.090	0.123	0.083	0.100	0.103
lb H_2O abs/lb O_2 produced	0.945	0.515	0.342	0.470	0.295	0.496	0.457
ΔP of canister (in. H_2O)	high	high	high	4	20	6	4
O_2 required (liters)[1]	292.8	298.4	328.3	503.5	348.4	246	182.5
O_2 produced (liters/lb)	47.0	87.3	67.7	91.3	63.3	57.5	28.4
CO_2 absorbed (liters/hr)	24.3	56.0	47.7	56.4	48.0	43.6	23.5

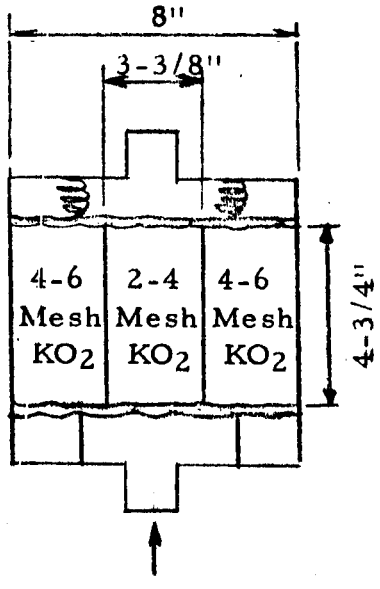
[1] Determined from actual simulator consumption and leakage.



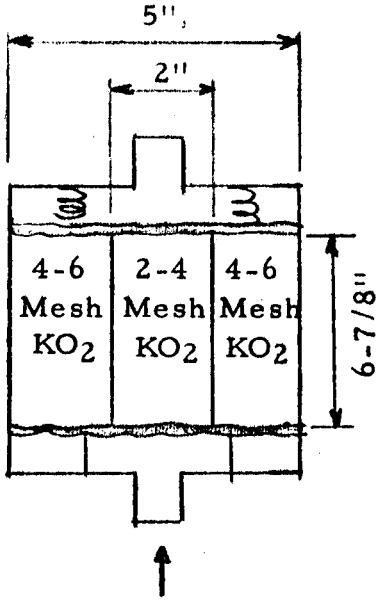
Flow
Run No. 35



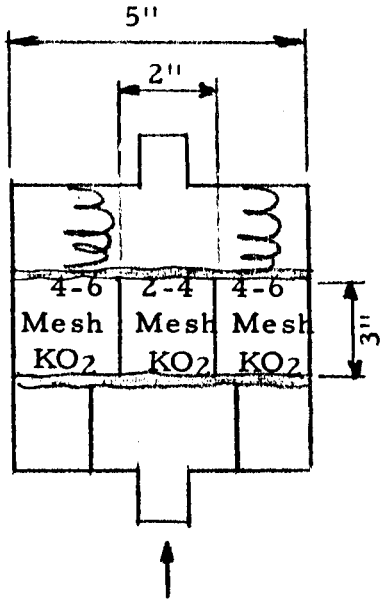
Flow
Runs No. 36 and 37



Flow
Run No. 38



Flow
Runs No. 39 and 40



Flow
Run No. 41

Fig. 1 - Canister Designs

RESULTS

Part 1

Run 35 - Sintered KO_2 in a 5 in. diameter canister was used in the system to provide a suitable atmosphere for three simulated men. The circulation rate through the canister was set at 8 SCM and the cooler outlet temperature was set at 50°F. The chemical started to react readily. However, the oxygen partial pressure could not be sustained and the CO_2 content started to build up. Increasing the flow rate and water content of the circulating stream, plus cooling the canister did not help the situation. However, the evolution and absorption rates were relatively constant throughout the run. Analysis of the chemical showed an oxygen efficiency of 30.5% and a chemical R.Q. of 0.573. Nevertheless, this run did show promise because the sintered chemical reacted readily. In gas mask experiments utilizing sintered KO_2, the chemical exhibited a tendency to not react readily and also react at a slow rate. However, it is felt, that, due to its potential and apparent advantages over regular potassium superoxide, further consideration should be given to it.

Part 2

Prior to performing runs at one-half atmosphere, a leakage rate was obtained on the system. Due to the rate being quite high for the first three runs, the system vacuum pump was used continually and its capacity was adjusted to balance the system pressure. Once this was established, the water content and oxygen partial pressure of the system were set at the desired levels and the run was started.

The first three runs were made with a system R.Q. of 0.503 and the last two with an R.Q. of approximately 0.8. In addition, the oxygen consumption rate per man was also varied.

Run 36 - This was the first run at one-half atmosphere using regular KO_2 in a 5 in. diameter canister to sustain the atmosphere for three simulated men each consuming 0.9 SCFH of oxygen and replenish the oxygen lost in leakage. A flow rate of 10 CFM and water partial pressure of approximately 12 mm Hg were the starting conditions.

Carbon dioxide absorption appeared to be very good until the pressure drop increased so much that the flow could not be maintained through the canister.

Oxygen production was not sufficient to overcome that used by the simulator and that lost by leakage. In addition, a low oxygen efficiency was obtained for the superoxide.

It is believed that an increased circulation rate through the chemical bed or a larger diameter bed would have resulted in better performance of the KO_2. Moreover, if the system R.Q. would have been approximately 0.7, the chemical would have supplied sufficient oxygen for the run.

Run 37 - The conditions for this run were altered such that the consumption rate was reduced to 0.77 SCFH per man, the initial water content of the system was reduced, and the initial flow rate through the bed was set at 8 CFM.

Oxygen production did not seem satisfactory at the start so the flow rate was increased to 10 CFM. This helped; but, again performance of the chemical was not sufficient for the requirements of the system and a low oxygen efficiency of the chemical again resulted. The KO_2 did, however, produce sufficient oxygen for consumption. Carbon dioxide absorption was very good for the chemical in this test.

Run 38 - For this run, the following changes were made: an 8 in. diameter canister was used to increase the oxygen production rate and reduce the pressure drop across the chemical bed, the flow rate through the bed was increased, and the consumption rate for three men was set at 0.85 SCFH each.

Again good CO_2 absorption occurred but insufficient oxygen was produced. Also, no significant increase in oxygen efficiency resulted above that of runs 36 and 37.

Run 39 - In this run, the leakage rate was reduced to give a system R.Q. of 0.8 and the oxygen consumption rate for three men was set at 0.96 SCFH.

The results showed an increase in oxygen efficiency of the chemical but an insufficient carbon dioxide absorption to maintain a low percentage in the system.

Run 40 - This run was identical to run 39 except that the oxygen consumption rate per man was reduced to 0.83 SCFH. The KO_2 did not perform as well as in the previous run. In addition difficulty occurred in maintaining a constant inlet temperature ot the bed and constant system pressure.

Part 3

Run 41 - A 5 in. diameter canister of KO_2 and a circulation rate of 6 CFM through the chemical was used to sustain two simulated men consuming 0.92 SCFH oxygen each.

The results showed that more water was added to the system than that added by the simulator which means that in the complex reactions of KO_2 free water is released into the system. This explains why more oxygen can be evolved from KO_2 when less than theoretical water is absorbed by the chemical and/or is present in the system. When KOH is formed in the initial reaction of KO_2 and H_2O, it reacts with CO_2. When reacting with CO_2 many products can be formed i.e., carbonates, bicarbonates, hydrates, free water, etc. The temperature of the canister bed may determine the nature of the products formed.

ANALYSIS OF RUNS

All the runs performed to date have indicated that only three major reactions take place in a bed of superoxide. These are the first three listed in Table 4. The others are minor and do not greatly affect the chemical performance.

Table 4 - Typical KO_2 Reactions

1.	$2KO_2 + H_2O$	$\longrightarrow$	$2KOH + 3/2\ O_2 + 9.4$ Kcal
2.	$2KOH + CO_2$	$\longrightarrow$	$K_2CO_3 + H_2O + 33.7$ Kcal
3.	$KOH + CO_2$	$\longrightarrow$	$KHCO_3 + 33.1$ Kcal
4.	$KOH + 3/4\ H_2O$	$\longrightarrow$	$KOH \cdot 3/4\ H_2O + 16.57$ Kcal
5.	$KOH + H_2O$	$\longrightarrow$	$KOH \cdot H_2O + 20.0$ Kcal
6.	$KOH + 2\ H_2O$	$\longrightarrow$	$KOH \cdot 2\ H_2O + 33.8$ Kcal
7.	$2\ K_2CO_3 + 1/2\ H_2O$	$\longrightarrow$	$K_2CO_3 \cdot 1/2\ H_2O + 15.2$ Kcal
8.	$K_2CO_3 + 1\text{-}1/2\ H_2O$	$\longrightarrow$	$K_2CO_3 \cdot 1\text{-}1/2\ H_2O + 22.77$ Kcal

During a run, the chemical therefore, reacts in the following manner: As the stream enters the bed, the moisture reacts with the superoxide producing oxygen and the hydroxide. Any carbon dioxide in the stream is then picked up by the hydroxide. At first the bicarbonate reaction is predominant as indicated by an analysis of zero percent CO_2 in the effluent

stream. As the CO_2 content increases in the exit stream, it shows that the reaction is progressing toward the carbonate reaction. The water formed here then either passes through the bed as a vapor, reacts with some unreacted superoxide or forms the hydrates listed in equation 4 to 8. Toward the end of the run, the oxygen evolution and CO_2 absorption decrease, indicating that the chemical is practically spent.

By utilizing the parameters of temperature, bed configuration, granule size, and the moisture and CO_2 content of the stream through the bed, the overall reaction of the chemical can be controlled to meet various system requirements as indicated below:

1. Oxygen evolution rate may be controlled by water content of the circulating stream, granule size and bed configuration.

2. Regulation of the temperature of the bed and the carbon dioxide partial pressure of the circulating stream will control the absorption characteristics of the chemical.

3. Control of pressure drop through a bed of superoxide may be accomplished by the design of the bed, size of the granule, and initial moisture content of the system.

CONCLUSIONS

Several conclusions that can be made as a result of runs during this quarter are:

1. Sintered KO_2 can be used in a closed system to provide a breathable atmosphere.

2. The use of sintered KO2 permits more water to be retained in the system.

3. KO_2 can be used in a system operating at one-half atmosphere without the need of auxiliary methods to remove CO_2 and water.

4. At low system R.Q.s, KO_2 performs extremely well.

5. While there are many short time reactions occurring in the canister it appears that the overall reaction is determined by the first three equations shown. (See Table 4).

FUTURE WORK

1. Continue work on the synthesis of CaO_4.

2. The surface area will be measured on additional KO_2 mixtures and NaO_2.

3. Perform runs at simulated altitude using sintered KO_2 and NaO_2 to provide a suitable environment in a closed system.

4. Perform additional simulated altitude runs varying conditions to improve KO_2 performance.

5. Determine the odor and contaminant removal characteristics of superoxides in a closed system operating at sea level and at simulated altitude.

6. Simulate space flights in which leaks occur and are repaired.

7. Obtain mass transfer coefficient correlations of superoxides.

8. Establish an equation for the determination of the minimum circulation rate requirement through a superoxide bed to provide a breathable atmosphere.